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ADHESIVE COMPOSITION
[Nenchakuzai soseibutsu]

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Specification /305*

1. Title of the Invention

ADHESIVE COMPOSITION

2. Claims

(1) An adhesive composition comprising (A) 100 ppw moisture-cured rubber organic polymer with at least one reactive silicon functional group in the molecule, (B) 0.1 to 50 ppw silicon compound with one silicon atom and two hydroxyl groups or hydrolyzable groups on the silicon atom and (or) a silicon compound with 2 to 20 silicon atoms, and at least one hydroxyl group or hydrolyzable group per silicon atom or a total of two to five silicon atoms, and (C) 5 to 120 ppw tackifier resin.

(2) The adhesive composition described in Claim 1, wherein the rubber organic polymer in (A) is an alkylene oxide polymer.

(3) The adhesive composition described in Claim 1, wherein the rubber organic polymer in (A) is a polypropylene oxide polymer.

(4) The adhesive composition described in Claim 1, wherein the rubber organic polymer in (A) is a copolymer in which one or more vinyl monomers have been polymerized in the presence of an alkylene oxide polymer.

(5) The adhesive composition described in Claim 1, wherein the rubber organic polymer in (A) is a copolymer in which one or more vinyl monomers have been polymerized.

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*Numbers in the margin indicate pagination in the foreign text.

(6) The adhesive composition described in Claim 1, wherein the reactive silicon group in (A) is a functional group expressed by the following formula:

(1) :

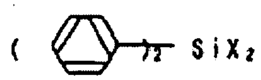
$$-\left[\begin{array}{c} R^{1}_{b} \\ | \\ Si-O \\ | \\ X_{2-b} \end{array}\right]_{n} - \begin{array}{c} R^{1}_{a} \\ | \\ SiX_{3-a} \end{array} \qquad (1)$$

(In this formula, R1 is a monovalent hydrocarbon group with 1 to 12 carbon atoms selected from among an alkyl group and aryl group, x is a hydroxyl group or hydrolyzable group, a is 0, 1, 2 or 3, b is 0, 1 /306
or 2, provided $1 \leq a+b \leq 4$, and n is 0 to 19.)

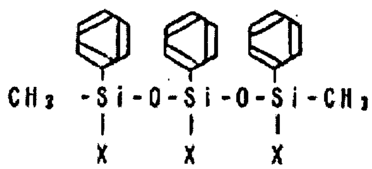
(7) The adhesive composition described in Claim 6, wherein the reactive silicon group in (A) is an alkoxysilyl group.

(8) The adhesive composition described in Claim 1, wherein the silicon compound in (B) has a phenyl group bonded to a silicon atom bonded to a hydroxyl group or hydrolyzable group.

(9) The adhesive composition described in Claim 8, wherein the silicon compound in (B) is expressed by one of the following formulas:

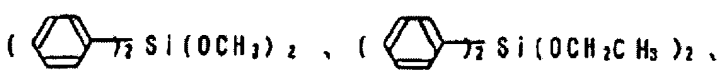


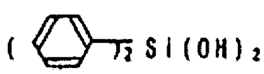
OR



(In these formulas, X is a hydroxyl group or hydrolyzable group.)

(10) The adhesive composition described in Claim 9, wherein the silicon compound in (B) is one of the following:





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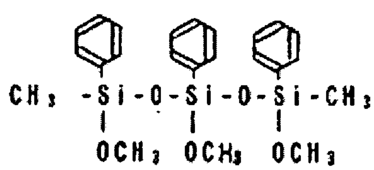


3. Detailed Description of the Invention

(Industrial Field of Application)

The present invention relates to a liquid cured adhesive composition with very good adhesive properties (tack, adhesive strength, retention strength).

(Prior Art and Problem Solved by the Invention)

Adhesives called pressure-sensitive adhesives have adhesive properties in which they adhere easily to the contact surface when slight pressure is applied with a finger tip.

Examples of applications for these adhesives include cellophane tape, vinyl tape for electrical insulation, masking tape, adhesive sheets and adhesive labels. The most commonly used polymer adhesives are diene or polyacrylic polymers. Because these polymers are solids or highly viscous liquids, a tackifier resin is added. But this makes the mixture difficult to apply to a base material such as tape, sheets and labels. Methods used to manufacture products with these adhesives (adhesive products) include the liquid adhesive method, emulsion adhesive method, and hot melt adhesive method.

The most common method is the liquid adhesive method. A monomer is added to a liquid monomer making it easy to handle. However, a large amount of organic solvent has to be removed, requiring special solvent removal equipment. Heat energy is required to evaporate the solvent, which increases costs. Therefore, this method is dangerous and hazardous in the work environment.

In order to solve this problem, non-liquid adhesives have been introduced such as acrylic emulsion adhesives and rubber hot melt adhesives. In the case of the former, emulsion polymerization is performed using an acrylic monomer as the emulsifier. The resulting aqueous emulsion is easy to handle, but it is not sufficiently hydrophobic and has an acrylic odor. In the case of the latter, a rubber polymer that is a lightly viscous liquid at high temperature is used. This can be used without a solvent, but there are problems with heat resistance and tack, which is an important property of adhesives. It is thus not satisfactory.

In order to overcome the problems with liquid, emulsion and hot melt adhesives, a liquid-cured adhesive has been proposed. /307

A liquid-cured adhesive has a low molecular weight before curing. As a result, it is only slightly viscous at room temperature. It is easy to handle and apply to a base material even though no solvent is used. After curing, it has a high enough molecular weight to be used as an adhesive. Several liquid-cured adhesives have been proposed. One of these is an adhesive composition having a rubber organic polymer with at least one reactive functional group (JP S59-71377A). The reactive silicon functional group in the rubber organic compound forms a siloxane bond and the adhesive becomes crosslinked and heavier in terms of molecular weight when moisture is applied during curing. When a tackifier resin is added, adhesiveness is manifested. This adhesive composition has good heat resistance and low temperature properties, but these properties are not adequate and need to be improved.

More specifically, an adhesive has three basic properties. The following three properties are essential.

(1) Adhesive Strength (The strength required to peel an adhesive product such as tape off a contact surface after sufficient pressure has been applied and time has passed. In general, it should be high.)

(2) Tack (The stickiness of an adhesive surface. In general, it should be high.)

(3) Retention Strength (Clip resistance. When pressure is applied to the base material in a direction parallel to the contact surface,

the amount of slippage in terms of length between the base material and the contact material. In general, it should be a short distance.)

When an adhesive composition consists of a rubber organic polymer with a reactive silicon functional group, it has to first have sufficient retention strength. When the amount of reactive silicon functional groups in the rubber organic polymer is increased, the number of crosslinking points increases during curing. It also has to achieve a sufficiently high molecular weight. Unfortunately, when the amount of reactive silicon functional groups is increased, the adhesive strength and tack decrease.

In order to improve low adhesive strength and tack, a tackifier resin is added. The adhesive strength is improved proportional to the amount of tackifier resin added. Standard adhesive strength is achieved by adding a large amount of tackifier resin. The tack is maximal a relatively low adhesive strength, i.e., when a low amount of tackifier resin has been added. It quickly deteriorates when tackifier resin is added. Therefore, when this composition is used, it is difficult to obtain a composition that has good adhesive strength and tack at the same time.

Because a tackifier usually has a low molecular weight, an unsaturated group and other functional groups, its properties largely depend on the temperature. Therefore, when a large amount of tackifier resin is added to obtain standard adhesive strength, both weather resistance and high temperature resistance decline.

If an adhesive with good adhesive strength and tack could be obtained with the addition of a relatively small amount of tackifier resin, it would be a very useful adhesive.

The purpose of the present invention is to solve this problem by providing an adhesive composition with sufficient adhesive properties even when a large amount of tackifier resin is added to a rubber organic polymer with a reactive silicon functional group.

(Means of Solving the Problem)

The present invention relates to an adhesive composition comprising (A) 100 ppw moisture-cured rubber organic polymer with at least one reactive silicon functional group in the molecule, (B) 0.1 to 50 ppw silicon compound with one silicon atom and two hydroxyl groups or hydrolyzable groups on the silicon atom and (or) a silicon compound with 2 to 20 silicon atoms, and at least one hydroxyl group or hydrolyzable group per silicon atom or a total of two to five silicon atoms, and (C) 5 to 120 ppw tackifier resin.

If this composition is used, an adhesive composition with very good adhesive strength and tack can be obtained even when a smaller /308 amount of tackifier resin is added compared to compositions without (B).

(Working Examples)

The polymer with a moisture-cured rubber organic polymer framework with at least one reactive silicon functional group in the molecule in (A) of the present invention can be an alkylene oxide polymer (polyether) polymerized with a cyclic ether such as

polypropylene oxide, ethylene oxide or tetrahydrofuran; a polyester condensation polymerized with a dibasic acid such as adipic acid or ring-opening polymerized with a lactone; an ethylene-propylene copolymer; a copolymer of polyisobutylene or isobutylene and isoprene; polychloroprene; a copolymer of polyisoprene or isoprene and butadiene, styrene and acrylonitrile; a copolymer of polybutadiene or butadiene and styrene and acrylonitrile; a polyolefin hydrogenated from a polymer of polyisoprene, polybutadiene or isoprene and butadiene; a polymer polymerized from one or more vinyl monomers including a polymer of a polyacrylic acid ester radical polymerized from vinyl monomers such as ethylacrylate or butylacrylate, or an acrylic acid ester and vinyl acetate, acrylonitrile, styrene and ethylene; a graft polymer in which a vinyl monomer is polymerized in the rubber organic polymer used in the present invention; and a polymer such as a polysulfide. Among these, the following are preferred: a polyalkylene oxide polymer such as polypropylene oxide with a repeating unit expressed by the following formula:

$$-R^2-O-$$

(In this formula, R^2 is a divalent alkylene group with 2-4 carbon atoms.), a polymer or copolymer such as a graft polymer obtained by polymerizing one or more vinyl monomer such as an acrylic acid ester, styrene, acrylonitrile or vinyl acetate in the presence of a polyalkylene oxide polymer such as polypropylene oxide, and a copolymer such as a polyacrylic acid ester or acrylic acid ester and vinyl acetate, acrylonitrile, styrene and ethylene able to readily

introduce a reactive functional group to a molecular terminus, able to be manufactured as a liquid polymer in no solvent, and able to readily manifest balanced adhesive characteristics. In order to be hydrophobic, inexpensive and easy to handle in liquid form, it should be a polymer whose main ingredients are propylene oxide and (or) acrylic acid alkyl ester, or a polymer containing 50% or more (weight percentage, same as below) propylene oxide and (or) acrylic acid alkyl ester.

The reactive silicon functional group contained in the rubber organic polymer can be a hydrolyzable silicon group or a silanol group.

In this specification, reactive silicon functional group means a group in which a hydrolyzable group able to be hydrolyzed with a hydroxyl group or water able, in turn, to undergo a silanol condensation reaction in the presence or absence of a silanol condensation catalyst, undergoes a condensation reaction with a silicon atom. An example is expressed by the following formula:

(1) :

$$-\left[\begin{array}{c} R^1_b \\ | \\ Si-O \\ | \\ X_{2-b} \end{array}\right]_n - \begin{array}{c} R^1_a \\ | \\ SiX_{3-a} \end{array} \qquad (1)$$

(In this formula, R1 is a monovalent hydrocarbon group with 1 to 12 carbon atoms selected from among an alkyl group and aryl group, x is a

hydroxyl group or hydrolyzable group, a is 0, 1, 2 or 3, b is 0, 1 or 2, provided $1 \leq a+b \leq 4$, and n is 0 to 19.)

Specific examples of hydrolyzable groups include a hydrogen atom, halogen atom, alkoxy group, acyloxy group, ketoxymate group, amino group, amide group, aminooxy group, mercapto group and alkenyloxy group. An alkoxy group is especially preferred because it is mildly hydrolyzable and easy to handle. These hydrolyzable groups can be /309 bonded to a single silicon atom in the 1 to 3 range. A preferred reactive silicon functional group has b = 2 and a = 0 or 1 among the reactive silicon functional groups expressed in Formula (1).

There should be one and even two or more silicon atoms forming the reactive silicon functional group. If the silicon atoms are bonded via siloxane bonds, up to 20 atoms can be used.

Any one of the following methods can be used to introduce the reactive silicon functional group to the rubber organic polymer.

(1) A method in which a monomer with a reactive silicon functional group and a copolymerizable unsaturated group in the molecule such as vinyl trialkoxysilane, methyacryloyloxypropylmethyl dialkoxy silane, and methacryloyloxypropyl trialkoxy silane is copolymerized with a polymerizable monomer such as ethylene, propylene, isobutylene, chloroprene, isoprene, butadiene and acrylic acid ester, or a method in which a monomer with a reactive silicon functional group and a copolymerizable epoxy group in the molecule such as gamma-glycydoxypropyltrimethoxysilane, gamma-glycidoxypropylmethyl dimethoxysilane is copolymerized with propylene

oxide or ethylene oxide. In these methods, the reactive silicon functional group can be introduced to a molecular side chain.

(2) A method in which a silicon compound with a reactive silicon functional group and a mercapto group and disulfide group that can undergo a chain transfer reaction with the reactive silicon functional group is polymerized with a radical polymerizable monomer using a chain transfer agent.

(3) A method in which a radical polymerizable monomer is polymerized using an azo or peroxide polymerization initiating agent containing a reactive silicon functional group such as azobis-2-(6-methyldiethoxysilyl-2-cyanohexane). In methods (2) and (3), the reactive silicon functional group is introduced to the polymer molecule terminus.

(4) A method in which a polymer is used with a functional group (Y functional group) such as a hydroxyl group, carboxyl group, mercapto group, epoxy group or isocyanate group in the side chain and (or) terminus of the polymer. A silicon molecule with a Y' functional group in the molecule reactable with the Y functional group and a reactive silicon functional group is reacted with the Y functional group. What follows are specific examples of reactions. The present invention is not limited to these examples.

Y Group in Polymer	Y' Group in Si Compound	Bond Created
$-COOH$	$HO-$	$-COO-$
"	$\underset{\diagdown O \diagup}{CH_2-CH-}$	$-COOCH_2\underset{OH}{CH}-$
"	H_3N-	$-COO^{\ominus}H_3\overset{\oplus}{N}-$
"	H_2N-	$-CONH-$
"	$OCN-$	$-COOCONH-$
"	$CH_2=CHCOO-$	$-COOCH_2CH_2COO-$
$-OH$	$OCN-$	$-OCONH-$
$-SH$	$\underset{\diagdown O \diagup}{CH_2-CH-}$	$-SCH_2\underset{OH}{CH}-$
"	$OCN-$	$-SCONH-$
"	$CH_2=CHCOO-$	$-SCH_2CH_2COO-$
"	$CH_2=CH-$	$-SCH_2CH_2-$
"	$Cl\ CH_2-$	$-SCH_2-$
$-\underset{\diagdown O \diagup}{CH-CH_2}$	$HOOC-$	$-\underset{OH}{CH}CH_2OCO-$
"	$HS-$	$-\underset{OH}{CH}CH_2S-$
"	H_2N-	$-\underset{OH}{CH}CH_2NH-$
"	$HO-$	$-\underset{OH}{CH}CH_2O-$
$-NH_2$	$\underset{\diagdown O \diagup}{CH_2-CH-}$	$-NHCH_2-\underset{OH}{CH}-$
"	$OCN-$	$-NHCONH-$
"	$HOOC-$	$-\overset{\oplus}{N}H_3\overset{\ominus}{O}CO-$ OR $-NHCO-$
"	$Cl\ CH_2-$	$-\overset{\oplus}{N}H_2\ CH_2-$ $\underset{}{Cl^{\ominus}}$
"	$CH_2=CHCOO-$	$-NHCH_2CH_2COO-$
$-\overset{O}{\overset{\Vert}{C}}NH_2$	$OCN-$	$-\overset{O}{\overset{\Vert}{C}}NHCONH-$
$-CH=CH_2$	$HS-$	$-CH_2CH_2S-$
"	$H-Si\equiv$	$-CH_2CH_2Si\equiv$
$-NCO$	$HOOC-$	$-NHCOOCO-$
"	$HO-$	$-NHCOO-$
"	$HS-$	$-NHCOS-$
"	H_2N-	$-NHCONH-$
$-CH-CH-$ with $O=C-O-C=O$ (anhydride ring)	$HO-$	$-\underset{O=\underset{OH}{C}}{CH}-\underset{\underset{O-}{C}=O}{CH}-$
"	H_2N-	$-\underset{O=\underset{OH}{C}}{CH}-\underset{\underset{NH-}{C}=O}{CH}-$

Preferred polymers with a Y functional group used as the initial or intermediate materials in the table include the following: polyetherpolyols with repeating units in which the main chain is essentially a repeating unit expressed by $-R^2-O-$ (where R^2 is a bivalent alkylene group with 2 to 4 carbon atoms) such as polyoxypropylenepolyol, polyoxyethylenepolyol, and polyoxytetramethylenepolyol; polyesterpolyols condensation polymerized

with a dibasic acid such as adipic acid and glycol or ring-opening polymerized with a lactone; polycarboxylic acids or polyols such as polyisobutylene; polycarboxylic acids or polyols of copolymers such as polybutadiene or butadiene and styrene and acrylonitriles; polyols of polyolefins obtained by hydrogenating polyisoprene or polybutadiene; polymers containing an isocyanate functional group obtained by reacting a polyol or polycarboxylic acid with polyisocyanate; and a polymer containing a vinyl unsaturated group obtained by reacting a polyol with a polyvalent halogen compound and a halogen compound containing a vinyl unsaturated group. Preferably, the Y functional group is on the molecule terminus.

Silicon compounds with a Y' functional group include silanes with amino groups such as gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl methyldimethoxysilane and gamma-aminopropyl triethoxysilane; silanes with mercapto groups such as gamma-mercaptopropyl trimethoxysilane and gamma-mercaptopropyl methyl dimethoxysilane; ethoxysilanes such as gamma-glycidoxypropyl trimethoxysilane, beta-(3,4-epoxycyclohexyl) ethyltrimethoxysilane; silanes with vinyl unsaturated groups such as vinyl triethoxysilane, gamma-methacryloyloxypropyl triethoxysilane /311
and gamma-acryloyloxypropylmethyl diemthoxysilane; silanes with chlorine atoms such as gamma-chloropropyl trimethoxysilane; silanes with isocyanate such as gamma-isocyanatopropyl triethoxysilane and gamma-isocyanatopropylmethyl dimetoxysilane; and hydrosilanes such as

methyldimethoxysilane, trimethoxysilane and methyldiethoxysilane. The present invention is by no means restricted to these examples.

When a polymer with a Y functional group is combined with a silicon compound with a Y' functional group, (I) a polymer with an isocyanate group can be combined with a silane containing an amino group or a silane containing a mercapto group, or (II) a polymer with a vinyl unsaturated group can be combined with a hydrosilane. In (II), a polypropyleneoxide with an allylether group on the molecule terminus is preferably combined with a hydrosilane. In (II), a vinyl group and hydrosilyl group should be reacted in a hydrosilyl reaction using a catalyst such as a platinum compound to introduce a silyl group to the polymer.

The molecular weight of the moisture-cured rubber organic polymer with one, preferably 1.4 to 6, reactive silicon functional groups in the molecule used as (A) in the present invention is usually 500 to 50,000, and preferably 3000 to 20,000, from the standpoint of an easy-to-handle liquid form. If the number of reactive silicon functional groups in the molecule is less than one, the curing is insufficient and problems with clip resistance occur.

In compounds of the present invention with at least one reactive silicon functional group in the molecule, the reactive silicon functional group should be on the molecule terminus.

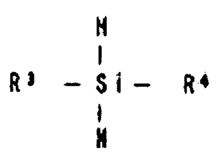
Specific examples of (A) include the compounds disclosed in JP45-36319B, JP46-12154B, JP49-32673B, JP50-156599A, JP51-73561A, JP54-6096A, JP55-13767A, JP54-13768A, JP55-82123A, JP55-123620A, JP55-

125121A, JP55-131021A, JP55-131022A, JP55-135135A, JP55-137129A, JP57-179210A, JP58-191703A, JP59-78220A, JP59-78221A, JP59-78222A, JP59-78223A and JP59-168014A. These are all effective, but the present invention is not restricted to these examples.

Component (B) in the present invention can be a silicon compound having one silicon atom with two hydroxyl groups or hydrolyzable groups on the silicon atom and (or) a silicon compound with 2 to 20 silicon atoms with one hydroxyl group or hydrolyzable group per silicon atom or a total of 2 to 5 hydroxyl groups or hydrolyzable groups.

The amount and reactivity of these silicon compounds are adjusted to the reactive silicon functional groups in the rubber organic polymer in (A) so that the structure of the rubber organic polymer is changed as appropriate for use as an adhesive.

The silicon compounds with one silicon atom are expressed by Formula (2):



(2)

In this formula, R1 is a monovalent organic group. These organic groups include a halogen atom, hydroxyl group, alkoxy group, nitrile group, amino group, mercapto group, acid amide group, carboxylic acid group, epoxy group and acrylonitrile group.

Specific examples of silicon compounds expressed by Formula (2) include the following:

$(CH_3)_2Si(OCH_3)_2$,

$(CH_3CH_2)_2Si(OCH_3)_2$, $(CH_3)_2Si(OCH_2CH_3)_2$,

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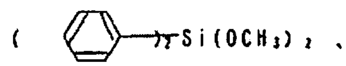
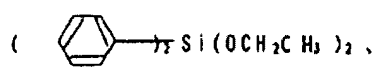
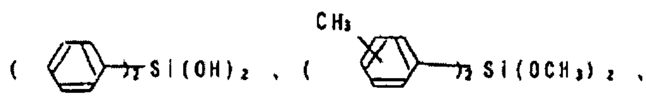
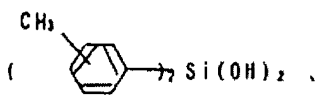
$(CH_3CH_2)_2Si(OCH_2CH_3)_2$,





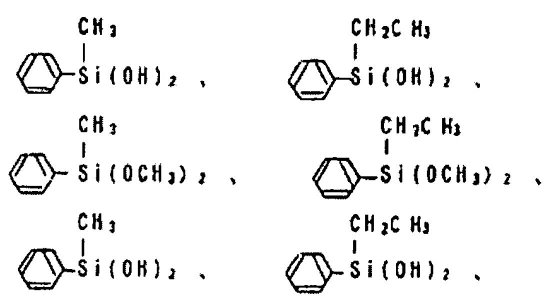


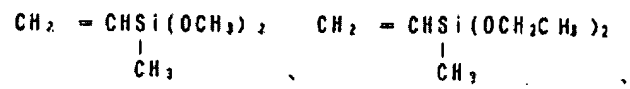


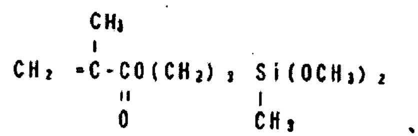
$(CH_3)_2Si(OCH_2CH_2OCH_3)_2$,

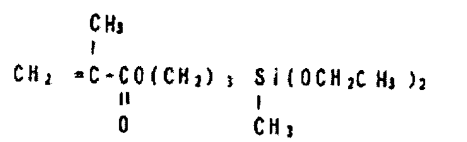
$(CH_3CH_2)_2Si(OCH_2CH_2OCH_3)_2$,

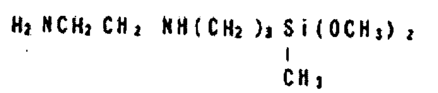
$(CH_3)(CH_3CH_2)Si(OCH_3)_2$,

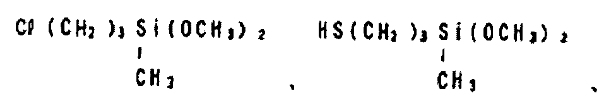


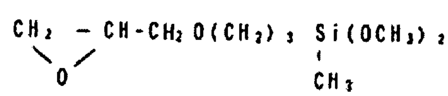










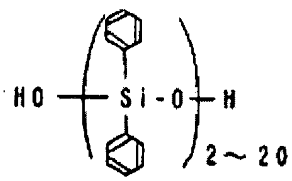


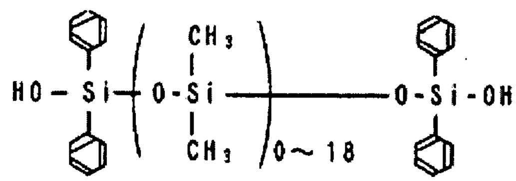
The present invention is not restricted to these examples.

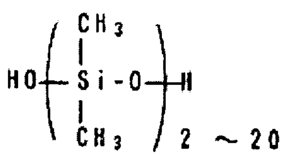
In addition to a compound with a single silicon atoms as expressed by Formula (2), specific silicon compounds with 2 to 20

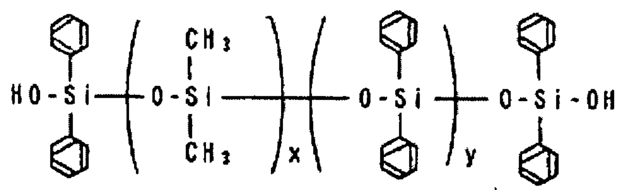
silicon atoms can be used as (B) in the present invention as explained above.

Specific examples of these silicon compounds include the following:

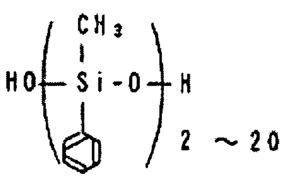


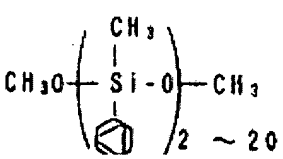


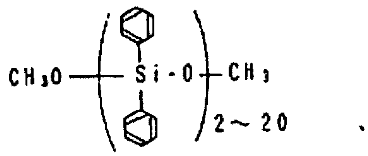


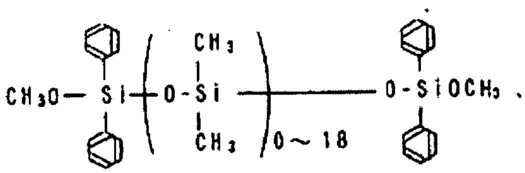


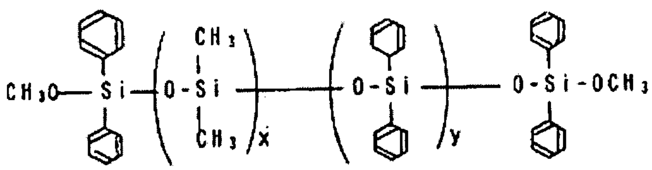
($x + y = 0 \sim 18$),





 、

 、



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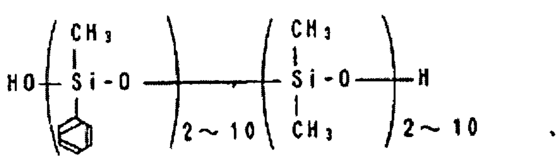
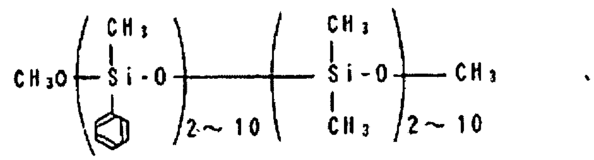
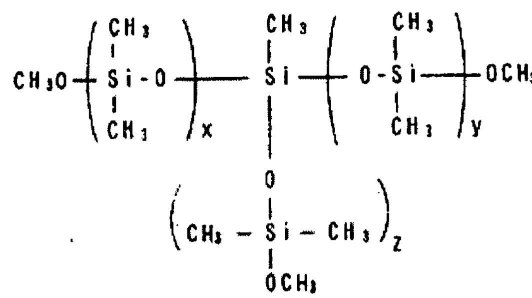
 、

 、



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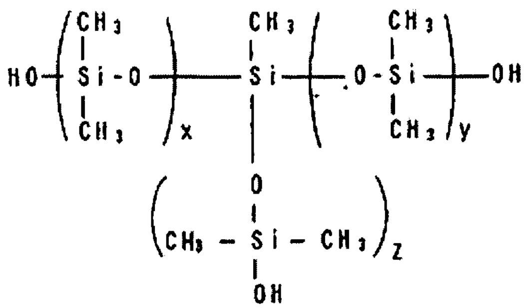

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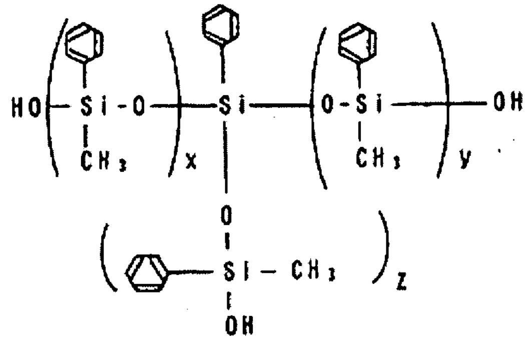
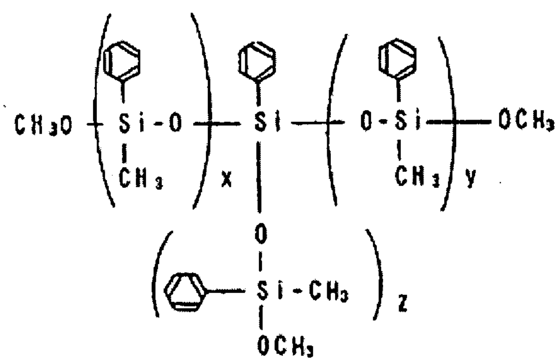
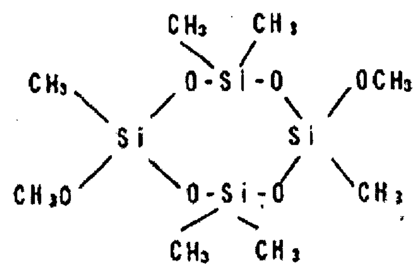


$(1 \leqq x + y + z \leqq 19)$ 、



$(1 \leqq x + y + z \leqq 19)$ 、



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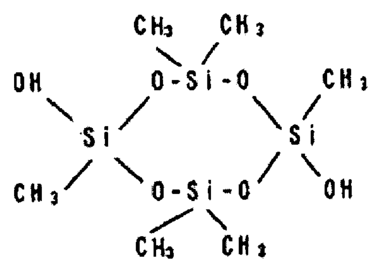

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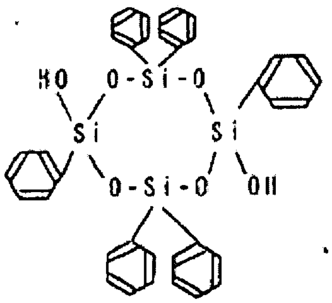
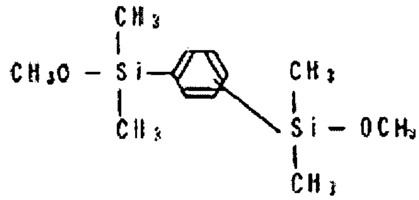
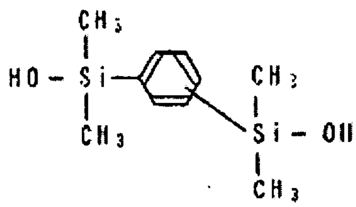
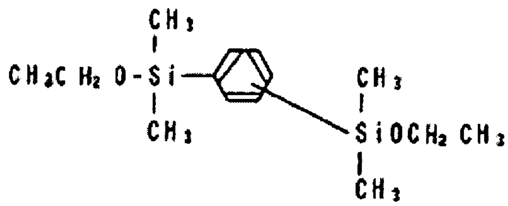




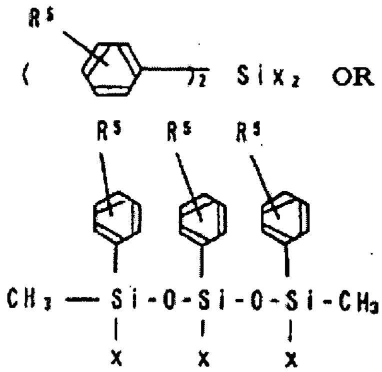




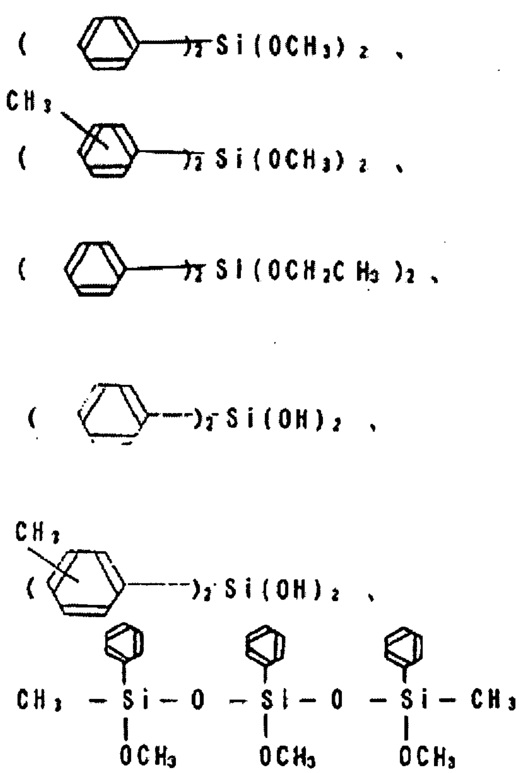
The present invention is not restricted to these examples.

Among the compounds used as (B), compounds with aryl groups such as phenyl groups, naphthyl groups and substituted phenyl groups, especially phenyl groups and tolyl groups, bonded to silicon atoms bonded to hydroxyl groups or hydrolyzable groups, and reacted selectively with the reactive functional groups in the rubber organic polymer in (A) not using a silanol condensation reaction are more stable in air and thus preferred.

These compounds have a big effect when the number of functional groups is nearly the same as the number of molecules. Five or fewer silicon atoms is preferred. Compounds expressed by the following formulas are especially preferred.



(In this formula, X is a hydroxyl group or hydrolyzable group, and R5 is a hydrogen atom or a hydrocarbon group with 1 to 5 carbon atoms.) Specific examples include the following:



The mechanism of the improved effect provided by the silicon compound in (B) is not well understood, but the actual effect is believed to vary.

First, by reacting the hydroxyl group or hydrolyzable group in the silicon atom in the silicon compound with the reactive silicon functional group on the rubber organic polymer in (A), the silicon compound in (B) is introduced to the rubber inorganic polymer and, after the reaction on the silicon atom in the silicon compound, the silanol group or hydrolyzable group can effectively undergo a chain extending, crosslinking or ring forming reaction with the reactive silicon functional group remaining in the rubber organic polymer. This is believed to result in a cured product with a crosslinking interpoint molecular weight and crosslinking density ideal for an /315
adhesive.

As for the number of hydroxyl groups or hydrolyzable groups on the silicon atoms in the silicon compound (B) used in the preset invention, it is two if there is one silicon atom in the compound, and one per silicon atom for a total of two to five if there is 2 to 20 silicon atoms in the compound. If there are too many hydroxyl groups or hydrolyzable groups on the silicon atoms, the crosslinking density of the cured compound is too high, and it is difficult to manifest sufficient adhesive properties. If there are too few groups, the chain extending reaction is given priority and the crosslinking density is too low. This results in a deterioration in retention strength and adhesive properties.

The amount of silicon compound (B) in the present invention depends on the long-term properties of the cured material and the number of silanol groups or hydrolyzable groups on the silicon atoms in the silicon compound. As for the reactive functional groups in the rubber organic polymer (A), the silanol groups or hydrolyzable groups in the silicon compound (B) should be 0.1 to 2 equivalent, preferably 0.3 to 1 equivalent. The actual amount used should be 0.1 to 5 parts, and preferably 0.3 to 20 parts, per 100 parts rubber organic polymer (A). Depending on the long-term properties, the silicon compounds (B) can be used alone or in combinations of two or more.

A tackifier resin is used as component (C) in the present invention, and there are no particular restrictions on the type of resin used. Examples include resins with polar groups such as rosin ester resins, phenol resins, xylene resins, xylenephenol resins and terpenephenol resins; petroleum resins such as low polarity aromatic resins, aliphatic-aromatic copolymers or alicylic resins; and common tackifier resins such as coumarone resins, low molecular weight polystyrene resins, and terpene resins.

Specific examples include low relative polarity resins such as Petrosin 80 (Mitsui Petrochemical), Neopolymer S (Nihon Petrochemical), Tack Ace A100 (Mitsui Petrochemical), Quinton 1500 (Nippon Zeon), FTR6100 (Mitsui Petrochemical), Picola Stick A75 (Hercules) and Cumarone G-90 (Nittetsu Chemical), and resins with polar groups such as YS Polystar T-115, YS Polystar S-145 (Yasuhara Yushi), Stebrite Ester 7 (Hercules) and Neopolymer E-100 (Nippon

Sekiyu Chemical). The present invention is not restricted to these examples.

The number of parts of tackifier resin (C) used depends on the type and amount. However, it is generally 5 to 120 parts and preferably 20 to 100 parts per 100 parts rubber organic polymer (A). If less than 5 is used, the adhesive strength and tack are insufficient. If more than 120 parts are used, good tack characteristics are difficult to obtain. Less than 100 parts is preferred.

A catalyst can be used to accelerate the curing reaction due to silanol condensation. Examples of curing resins include organic tin compounds such as dibutyl tin dilaurate, tin diocylate, dioctyl tin maleate and phthalic acid reaction products, and dibutyl tin diacetyl acetate; the zirconium and aluminum compounds disclosed in JP59-183097A such as di-n-butoxyzirconium diacetyl acetate, n-butoxy zirconium triacetyl acetate, diisopropoxy aluminum acetyl acetate, aluminum triacetyl acetate, diisopropoxy aluminum ethyl acetate and aluminum triethyl acetoacetate; a metal salt of a carboxylic acid such as alkyl titanate; an amine such as dibutylamine-2-ethylhexoate; and other acidic and basic catalysts normally used as silanol condensation catalysts. The amount of catalyst used is normally 0.1 to 20 parts per 100 parts rubber organic polymer (A). If less than 0.1 parts is /316
used, the catalytic effect is low. If more than 20 parts is used, the curing occurs too quickly and application to the support material is difficult.

Other additives can be included if necessary. These include plasticizers and softeners such as dioctyl phthalate, butylbenzyl phthalate, polypropylene glycol, chlorinated paraffin and liquid polybutadiene; fillers such as calcium carbonate, clay, talc, titanium oxide, zinc oxide, silica, diatomaceous earth and barium sulfide; antioxidants; UV absorbers; pigments; and surfactants.

A solvent can be added to improve workability and lower viscosity. Examples include aromatic hydrocarbon solvents such as toluene and xylene, ester solvents such as ethyl acetate, butyl acetate, amyl acetate and cellosolve acetate; and ketone solvents such as methylethyl ketone, methylisobutyl ketone and diisobutyl ketone.

The following is an explanation of the method used to manufacture the composition of the present invention.

Generally, there are two methods for manufacturing the composition of the present invention.

The first method is to simply add the silicon compound (B) to a mixture containing the rubber organic polymer (A).

The heating and stirring conditions are adjusted to the properties of the silicon compound so that it is evenly dispersed and dissolved. It does not have to be completely transparent. It can be well dispersed despite being non-transparent. If necessary, a dispersion improving agent such as a surfactant can be added.

The second method is to react the silicon compound (B) with the rubber organic compound (A). If necessary, an acidic or basic catalyst such as a tin catalyst or titanic acid ester catalyst can be added. If

the compound has a hydrolyzable group in the silicon atom in the silicon compound, the necessary amount of water is added and heated under reduced pressure.

Specific examples of catalysts that can be used include titanic acid esters such as tetrabutyl titanate and tetrapropyl titanate; organic tin compounds such as dibutyl tin dilaurate, dibutyl tin maleate, dibutyl tin diacetate, tin octoate and tin naphthenate; zinc octylate; amines and carboxylic acid salts thereof such as butyl amine, octyl amine, dibutyl amine, monoethanol amine, diethanol amine, triethanol amine, diethylene triamine, triethylene tetraamine, oleyl amine, octyl amine, cyclohexyl amine, benzyl amine, diethylaminopropyl amine, xylylene amine, triethylene diamine, guanidine, diphenyl guanidine, 2,4,6-tris (dimethylaminomethyl) phenol, morpholine, N-methyl morpholine and 1,3-diazabicyclo (5,4,6) undecene-7 (DBU); low molecular weight polyamide resins obtained from excess polyamine and a polybasic acid; the reaction product of excess polyamine and an epoxy compound; and a silanol condensation catalyst such as a silane coupling agent with an amino base, gamma-aminopropyl trimethoxysilane and N-(beta-aminoethyl) aminopropyl methylmethoxysilane. These can be used alone or in combinations of two or more.

Because of its adhesive strength and tack, the adhesive composition of the present invention has a wide range of applications, including on tape, sheets, labels and foil. The adhesive composition can be applied in non-solvent liquid form, solvent form, emulsion form or hot melt form on a base material such as a synthetic resin or

modified natural resin film, paper, cloth, metal foil, metalized plastic, asbestos or fiberglass. When exposed to water or moisture, it can be cured at room temperature or using heat.

The following is a more detailed explanation of the adhesive composition in the present invention with reference to working examples.

Synthesis Example 1 /317

800 g of polypropylene oxide with an average molecular weight of 8000 and an allyl ether group on 90% of the termini was added to a pressure-resistance reaction chamber with a stirrer. 20 g of methyl dimethoxysilane was added, followed by 0.34 ml of platinum chloride catalytic solution (8.9 g of $H_2PtCl_6 \cdot 6H_2O$ dissolved in 18 ml of isopropyl alcohol and 160 ml of tetrahydrofuran), and the mixture was reacted for six hours at 80°C. The reaction rate was quantified from a gas chromatogram and an IR spectrogram. The result was a polypropylene oxide with 88% of the termini reacted and the following group at 81% of all termini.

$$(CH_3O)_2\overset{\displaystyle CH_3}{\overset{|}{Si}}-CH_2CH_2CH_2O-$$

Synthesis Example 2

90 g of the polypropylene oxide polymer with reactive silicon functional groups synthesized in Synthesis Example 1 with the following group at 81% of the termini and an average molecular weight of 8000 was added to a reaction chamber.

$$(CH_3O)_2\overset{\displaystyle CH_3}{\overset{|}{Si}}-CH_2CH_2CH_2O-$$

After the pressure was reduced and the chamber purged with nitrogen, the mixture was heated to 110°C and stirred. A mixture of separately prepared n-butylacrylate (30.9 g), gamma-methacryloxypropyldimethoxy methylsilane (0.3 g) and AIBN (0.3 g) was added dropwise in a nitrogen atmosphere over the course of an hour. Another 0.0015 g AIBN was dissolved in four times the amount of acetone and added after 15 minutes and after 30 minutes. The stirring was continued for another 30 minutes, and the polymerization reaction ended.

The resulting polymer was a pale yellow and clear viscous liquid. The amount of residual monomer was 1% in a GC analysis, and the viscosity was 540 P (B-type viscometer, 23°C).

Synthesis Example 3

100 g n-butylacrylate, 1.64 g gamma-methacryloxypropyl methyl dimethoxysilane, 2.11 g gamma-mercaptopropyl methyl dimethoxysilane and 0.33 g neopentyl glycol diacrylate were mixed together. 0.26 g AIBN was added, and the mixture stirred together and dissolved. 30 g of this mixture was added to a 300 ml four-mouth flask with a cooling tube, drop route and stirrer purged with dry nitrogen gas. This flash was heated in a nitrogen atmosphere in an oil bath (80°C). After several minutes, polymerization began and heat was generated. The contents became more viscous. After the heat subsided, the rest of the mixture was added gradually via the drop route. The entire amount was

added after approximately three hours. 60 µl of 20% acetone solution with AIBN was added after 15 minutes and after 30 minutes. The heat and stirring were continued for another 30 minutes, and the polymerization reaction was completed.

The resulting polymer was a colorless, clear, viscous liquid. The amount of residual monomer was 1.5% in a GC analysis, and the viscosity was 300 P (B-type viscometer, 23°C).

Working Examples 1-12 and Comparative Examples 1-9

100 parts polypropylene oxide with reactive silicon functional groups obtained in Synthesis Example 1, a silicon compound from Table 1 in the amount indicated in Table 1, 1 part Noclac NS-6 (Ouchi Shinko Chemical) antioxidant, tackifier resin (YS Polystar T-115 from Yasuhara Yushi with a softening point of 115°C dissolved in toluene to obtain a 60% solution) in the amount indicated in Table 1, and the appropriate amount of toluene were added together and dissolved thoroughly to obtain a solution with 60% solid component. 3 parts dibutyl tin diacetonate curing catalyst was added to the polypropylene oxide and mixed well using a spatula.

The resulting composition was applied to a 25 µm-thick polyester base (Luminar film manufactured by Toray) using a coater to obtain a film thickness of 25 µm when dry. This was heated for 3 to 5 minutes at 120°C using forced hot air.

The viscosity characteristics were tested using the following methods.

(Tack)

This was measured using the J. Dow tumbling ball tack method. The maximum diameter of the balls (x 1/32 in.) stopped after traveling a distance of 10 cm at an inclination angle of 30° and at a temperature of 23°C was indicated.

(Retention Strength)

It is applied to a 25 mm x 25 mm area on a stainless steel /318
plate, static weight is applied at 100°C using a 1 kg weight, and the distance is measured after 60 minutes.

(Adhesive Strength)

It is applied to a stainless steel plate and released after 24 hours at 23°C. The peeling rate at 180°C and a tensile speed of 300 mm/min was measured.

Table 1

W.E. No.	Si Compound Type	ppw	YS Polystar T-115 (pts)	Tack	Retention Strength (mm)	Adhesive Strength (g/cm)
1	$Ph_2Si(OH)_2$	2	60	32<	0	450
2	"	"	80	22	0	650
3	"	"	100	13	0	900
4	$Ph_2Si(OCH_3)_2$	4	60	27	0	400
5	"	"	80	16	0	600
6	"	"	100	11	0	900
7	$CH_3-Si(Ph)(OCH_3)-O-Si(Ph)(OCH_3)-O-Si(Ph)(OCH_3)-CH_3$	10	60	27	0	370
8	"	"	80	16	0	620
9	"	"	100	10	0	860
10	$(CH_3)_2Si(OCH_3)_2$	"	60	23	0	250
11	"	"	80	12	0	430
12	"	"	100	8	0	750
C.E. No. 1	–	–	60	21	0	230
" 2	–	–	80	10	0	400
" 3	–	–	100	5	0	660
" 4	$(CH_3)_3SiOH$	10	60	20	0	250
" 5	"	"	80	10	0	410
" 6	"	"	100	5	0	650
" 7	$CH_3Si(OCH_3)_3$	"	60	15	0	170
" 8	"	"	80	6	0	330
" 9	"	"	100	3	0	550

As is clear from the results for Comparative Examples 1 through /319
3 in Table 1, tack and adhesive strength deteriorate when the silicon compound in (B) is not used. The results from a silicon compound bonded to a phenyl group bonded to a silicon atom with a hydroxyl group or methoxy group are significant. As shown in Comparative Examples 4-9, the results are not good if too many or too few hydroxyl groups or methoxy groups are used.

Working Examples 13-22 and Comparative Examples 10-14

Compositions were prepared and evaluated as in Working Examples 1-12, except that the silicon compounds, tackifier resins and amounts in Table 2 were used. The results are shown in Table 2.

In Table 2, YS Polystar S-145 is a terpene phenol resin made by Yasuhara Yushi Co. Ltd. with a melting point of 145°C. FTR6100 is a petroleum resin made by Mitsui Petrochemical Co. Ltd. with a melting point of 97°C. Picola Stick A-75 is a styrene resin made by Hercules Inc. with a melting point of 75°C. Quinton 1500 is an ester-denatured alicyclic resin made by Japan Zeon Co. Ltd. with a melting point of 100°C, and Neopolymer E-100 is a petroleum resin made by Nihon Petrochemical Co. Ltd. with a melting point of 90°C.

Table 2

W.E. No.	Si Compound		Adhesive Resin		Tack	Retention Strength (mm)	Adhesive Strength (g/cm)
	Type	Amt (pt)	Type	Amt (pt)			
13	$Ph_2Si(OH)_2$	2	YS Polystar S-145	40	30	0	380
14	"	"	"	60	17	0	550
15	"	"	FTR6100	60	25	0	250
16	"	"	"	80	20	0	350
17	"	"	Picola Stick A-75	60	27	0	200
18	"	"	"	80	17	0	300
19	"	"	Quinton 1500	60	27	0	340
20	"	"	"	80	15	0	600
21	"	"	Neopolymer E-100	60	27	0	400
22	"	"	"	80	20	0	700
CE No 10	-	-	YS Polystar S-145	60	13	0	330
11	-	-	FTR6100	80	15	0	200
12	-	-	Picola Stick A-75	80	13	0	120
13	-	-	Quinton 1500	80	10	0	330
14	-	-	Nepolymer E-100	80	10	0	280

As is clear from the results in Table 2, the adhesive properties are improved when the silicon compound in (B) is used. The present invention is understood to be a technology applied to an adhesive in this range.

Working Examples 23-40 and Comparative Examples 15-32

The same method described in Working Examples 1-12 was applied using the rubber organic polymers in Synthetic Examples 2 and 3 to produce an adhesive tape, and the adhesive properties (tack, retention strength, adhesive strength) were measured. The results from the polymers in Synthetic Example 2 are shown in Table 3, and the results from the polymers in Synthetic Example 3 are shown in Table 4.

For the sake of comparison, results from an example where no silicon compound was added and results from an example where a silicon compound other than the ones in the present invention are shown in Table 3 and Table 4. The results of a performance evaluation using only commercially available adhesive product levels are shown in Table 5.

Table 3 /320

W.E. No.	Si Compound Type	ppw	YS Polystar T-115 (pts)	Tack	Retention Strength (mm)	Adhesive Strength (g/cm)
23	Ph_2 $Si(OH)_2$	2	60	29	0	350
24	〃	〃	80	17	0	550
25	〃	〃	100	10	0	850
26	Ph_2 $Si(OCH_3)_2$	4	60	30	0	400
27	〃	〃	80	15	0	620
28	〃	〃	100	9	0	900
29	$(CH_3)_2Si(OCH_3)_2$	10	60	20	0	270
30	〃	〃	80	11	0	430
31	〃	〃	100	6	0	700
C.E. No.						
15	–	–	60	15	0	240
〃 16	–	–	80	9	0	390
〃 17	–	–	100	4	0	650
〃 18	$(CH_3)_3SiOH$	10	60	17	0	230
〃 19	〃	〃	80	10	0	410
〃 20	〃	〃	100	5	0	630
〃 21	$CH_3Si(OCH_3)_3$	〃	60	11	0	160
〃 22	〃	〃	80	6	0	300
〃 23	〃	〃	100	2	0	520

Table 4

W.E. No.	Si Compound Type	ppw	YS Polystar T-115 (pts)	Tack	Retention Strength (mm)	Adhesive Strength (g/cm)
32	$Ph_2Si(OH)_2$	2	60	28	0	380
33	〃	〃	80	18	0	570
34	〃	〃	100	7	0	910
35	$Ph_2Si(OCH_3)_2$	4	60	25	0	350
36	〃	〃	80	20	0	560
37	〃	〃	100	10	0	850
38	$(CH_3)_2Si(OCH_3)_2$	10	60	17	0	270
39	〃	〃	80	10	0	460
40	〃	〃	100	4	0	740
C.E. No. 24	–	–	60	14	0	230
〃 25	–	–	80	8	0	380
〃 26	–	–	100	4	0	670
〃 27	$(CH_3)_3SiOH$	10	60	13	0	200
〃 28	〃	〃	80	10	0	300
〃 29	〃	〃	100	3	0	610
〃 30	$CH_3Si(OCH_3)_3$	〃	60	9	0	150
〃 31	〃	〃	80	4	0	270
〃 32	〃	〃	100	2	0	450

Table 5 /321

Commercial Adhesive Tape	Tack	Retention Strength (mm)	Adhesive Strength (g/cm)
Craft Tape (Rubber-Based)	17	5.5	330
Cellophane Tape (Rubber-Based)	14	5.5	290
Polyester Tape (Acrylic-Based)	7	0	420
Double-Sided Tape (Acrylic-Based)	9	0	550

* Retention strength measured at 40°C.

(Effect of the Invention)

The composition of the present invention has good retention strength, adhesive strength and tack at the same time when used as an

adhesive. It has sufficient adhesive properties even when containing very little tackifier resin.